PYROLYSIS OF RADIOACTIVE AND HAZARDOUS WASTE

- EXPERIENCE WITH A SAFE TECHNIQUE -

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ABSTRACT

The NUKEM pebble bed pyrolysis process, originally developed for the decomposition of spent solvent, has been adapted in the last years for the decomposition of spent resins and halogenated hydrocarbons. The process has been proven to be a simple and safe way for the treatment of the wastes during 5,500 hours total operating time. Low amounts of secondary waste and high decontamination factors were achieved. It became the reference process for German and French nuclear reprocessing as well as for the central non-nuclear hazardous waste treatment plant in the German state of Hesse.

INTRODUCTION

The pebble bed pyrolysis process has been developed by NUKEM originally for the decomposition of spent solvent during the years 1978 until 1981. Since 1981, a full-scale pilot plant has operated about 5,500 hours in total at NUKEM's R&D-facilities. In the meantime, the process has been adapted successfully for the decomposition of spent resins (1981 - 1984) and chemical hazardous waste (halogenated hydrocarbons, 1983 - 1986). It became the reference process for German and French nuclear reprocessing (pyrolysis of spent solvent Tributyl-phosphate, TBP and for the central hazardous waste treatment plant in the German state of Hesse.

BASIC PROCESS DESCRIPTION

TBP/Kerosene

A suspension of TBP/kerosene, water and calcium hydroxide is fed in an electrically-heated reactor, filled with Al_2O_3-balls. The TBP decomposes on the ball surface at about 400°C, forming calcium-pyrophosphates, as well as butene and butanol. The volatile components as well as the kerosene vapor are filtered by sintered metal filter candles and are drawn to the afterburner. The "ash" (Ca-phosphates) produced is milled down from the surface of the filler bodies by slow agitating and leaves the reactor in the form of a free-flowing powder through a grate at the bottom.

Spent Resins

The decomposition of spent organic resins is performed in the same reactor type at a temperature range of 200 - 350°C. The gaseous pyrolysis products (sulfur - and nitrogen-containing organic compounds, SO_2, NH_3, hydrocarbons and H_2O) leave the reactor via filter candles. The pyrolized particles are collected at the bottom as a black, freely-flowing inert product consisting mainly of carbon. The radionuclides contained in the spent resin remain in the ash resulting in high decontamination factors.

Halogenated Hydrocarbons (HHC)

For the chemical-thermal decomposition of HHC, the reactor is filled with porous calcium silicate granules instead of Al_2O_3-balls. The HHC are decomposed completely at a temperature range of 700 - 800°C. The contained halogens (Cl, F) are chemically bound to the calcium silicate thus excluding the possibility of generating secondary HHC like polychlorinated dioxines.

Laboratory and full-scale tests resulted in an overall decomposition efficiency of more than 99.999% for various HHC's like perchlorethylene, trichlorbenzene, polychlorinated biphenyls and fluorine containing HHC's.

The solid products are calcium chloride and carbon containing calcium silicates. The gaseous products drawn to the afterburner are chlorine free hydrocarbons, carbon monoxide and water.

Afterburner

The pyrolysis gases are drawn through an electrically-heated line to the afterburner, where the combustible components are burned with excess air.

An auxiliary gas burner, integrated in the main burner, ensures the required minimum temperature of 900°C (1,200°C in the case of processing HHC) in the burner chamber.

Instead of a gas burner, in the pilot plant an electrically-heated burner has also been used for minimizing the off-gas rate in the case of nuclear waste treatment. The upper limit for the burner temperature of 1,300°C is maintained by feeding excess air.

Flue Gas Treatment

The flue gas leaves the afterburner at temperatures of

900 to 1,300°C. The cooling of the flue gas proceeds by injection of water directly in the flue gas stream (quenching). The necessary water distribution is achieved by special two-media nozzles. The temperature control is obtained by changing the quantity of water.

The flue gas which leaves the cooling stage still contains such gases as NO_x, SO_x and about 0.1% of the initial radionuclides in the form of aerosols. The gases and solid substances (the size range is less than 3 μu) are removed in the next process stage. The flue gas is rapidly cooled down below 100°C in the inlet of the scrubber. The scrubbing solution is continuously circulated by means of a pump. The off-gas is further cleaned in the second scrubber (high efficiency scrubber). In the second scrubber, the off-gas is scrubbed by fresh water, which is then used for quenching. In this way it is guaranteed that clean off-gas always meets fresh scrubbing solution.

In the cooling and scrubbing stages, off-gas saturation with water takes place. Because of the material of construction of the HEPA-filters, the off-gas has to be preheated in order to avoid condensation of water inside the filters. Preheated air (ca. 300°C) is continuously added to the off-gas so that the off-gas temperature can still be kept 15 - 30oK above the dew point of the off-gas. The polishing filtration of the cleaned off-gas proceeds at a temperature of 90 to 110°C. The off-gas draft fans are installed downstream from the HEPA-filters. The necessary pressure drop is in the range of 20,000 to 35,000 Pa. For this purpose, rotary piston blowers are used.

OPERATING DATA

The main operating data of the NUKEM pilot plant are given in the following tables (1-3).

SUMMARIZED RESULTS

The following main process characteristics could be confirmed during 5,500 operating hours:

- Low corrosion rate because of low temperatures and "in-situ" neutralization by $Ca(OH)_2$ even for chlorine- and fluorine-containing wastes.
- High decontamination factors even for Cs and Ru because of low temperatures and oxygen-free atmosphere.
- High filtration efficiency in the first process stage resulting in an extreme low radioactive load of the off-gas treatment system.
- Excellent decomposition efficiency for halogenated hydrocarbons.
- Low sensitiveness to waste impurities and feed composition variations.
- Low amount of secondary waste and good cementability of the solid products.

TABLE I
Pebble Bed Reactor

	TBP	Resins	HHC
Total height (m)	1.5	1.4	2.0
Level of filler bodies (m)	1.2	1.2	1.9
Diameter (m)	0.6	0.6	0.6
Wall temperature (°C)	550	600	750
Bed temperature (°C)	400	500	750
Gas residence time (s)	5-9	5-10	20
Decomposition efficiency (%)	99.9	----	99.999

TABLE II
Mass Balance

Feed Rate (kg/hr)	Ash (kg/hr)	Rate
TBP/kerosene 30/70 (v/v)	30	5.4
TBP/kerosene 90/10 (v/v)	17	8.0
Spent resins (50 % H_2O)	25	3-6
HHC	20-30	70-110

TABLE III
Decontamination Factors (Reactor Including Filter Candles)

Cs, Eu:	105 *
Zr, Ru, Sr:	104 *
Organic Iodine:	5 - 20

* Detection limit